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[20] Crystal data for [(D)-isoG **1**]$_5 \cdot Cs^+ \cdot$ [(L)-isoG **1**]$_5Ph_4B^-$: $[(C_{19}H_{31}N_5O_5Si)_{10} \cdot Cs] \cdot B(C_6H_5)_4 \cdot 14\,NCCH_3$, $M_r = 5402.66$, crystal dimensions $0.724 \times 0.268 \times 0.192$ mm^3, monoclinic, space group $P2_1$, $a = 18.844(2)$, $b = 35.984(4)$, $c = 22.193(3)$ Å, $\beta = 92.027(5)°$, $V = 15{,}039(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.193$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.239$ mm^{-1}. Data were collected on a Bruker SMART 1000 CCD diffractometer at 193(2) K. The structure was determined by direct methods.[21] Refinement, using the SHELXL program,[22] was done to convergence on F^2 with $R(F) = 0.0907$% and $wR(F^2) = 0.1936$% for 39328 independent reflections. More information can be obtained from the Supporting Information. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144859. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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Synthesis and Characterization of Iron Silasesquioxane Phosphane Complexes**

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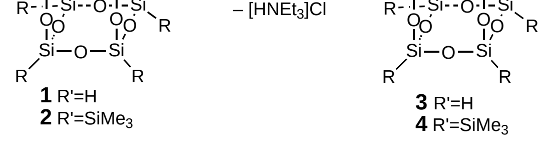
Iron centers supported on inorganic silicate matrices have been shown to be very active for the catalytic reduction of nitrogen oxides (NO_x)[1] and the selective oxidation of hydrocarbons using nitrous oxide. In the latter case, a purported iron–oxo species supported on an inorganic zeolite matrix has been shown to insert rapidly and cleanly into the C–H bonds of methane and benzene in the presence of N_2O as the oxidant.[2] In our studies of the catalytic chemistry of framework and extra-framework (ion-exchanged) metal-ion substituted zeolites we are interested in the development of soluble analogues of these iron silicates. Thus we have focused our attention on the synthesis and characterization of iron complexes of polyhedral silasesquioxanes (POSSs). Herein, we report the first structurally characterized iron–silasesquioxane complexes substituted into the silicate framework; the Fe centers are protected from oligomerization by a phosphane ligand. We have also delineated a reaction pathway that removes a phosphane ligand from a Fe^{III}–POSS complex to form a dimeric μ-oxo diiron complex. These compounds are of interest as homogeneous models for the heterogeneous iron zeolite catalysts.

Feher and co-workers have elegantly demonstrated that incompletely condensed polyhedral silasesquioxanes can serve as homogeneous models for both silica surfaces and zeolites, which is possible because of their flexible Si–O frameworks and defined cagelike structures.[3] A number of metal–silasesquioxane complexes have been synthesized and characterized as models of heterogeneous catalysts. For example, titanium–silasesquioxane complexes can efficiently catalyze the liquid-phase epoxidation of olefins,[4] thereby modeling the reactivity of heterogeneous titanasilicate (for example TS-1[5]) catalysts. Analogously, soluble iron–silicate compounds might model the heterogeneous iron–zeolite catalysts; however, no Fe–POSS complexes have been reported. Reactions of simple iron salts with POSS and similar analogues lead to mixtures that have been difficult to characterize,[6] although dimeric POSS complexes have been reported for several other metals.[3b] Our approach to making molecular Fe–POSS complexes has centered on protecting iron centers from oligomerization by the use of simple phosphane ligands. This approach is similar to that used by Lugmair and Tilley to synthesize the soluble monomeric iron silicate $[Fe\{OSi(O\mathit{t}Bu)_3\}_3] \cdot THF$ in which the steric bulk of the organosilicate ligand is used to prevent oligomerization.[7]

We have employed both the incompletely condensed POSS **1** and its trimethylsilyl mono-protected analogue **2** to support iron centers. Reactions of the iron(II) precursor $[FeCl_2(dcpe)]$ (dcpe = bis(dicyclohexylphosphanyl)ethane) with **1** or **2** in the presence of triethylamine in benzene afforded the iron(II)-(dcpe)–silasesquioxane compounds **3** and **4**, respectively (Scheme 1), which were isolated in high yield as colorless crystals. The iron(III) analogue **5** was prepared and isolated in a similar manner from the reaction of $[FeCl_3(PCy_3)]$ (Cy = cyclohexyl) and **1** (Scheme 2, top). Complexes **3**–**5** are paramagnetic and give broad signals in the NMR spectra.



Scheme 1. Synthesis of the mono iron compounds, $R = c\text{-}C_5H_9$.

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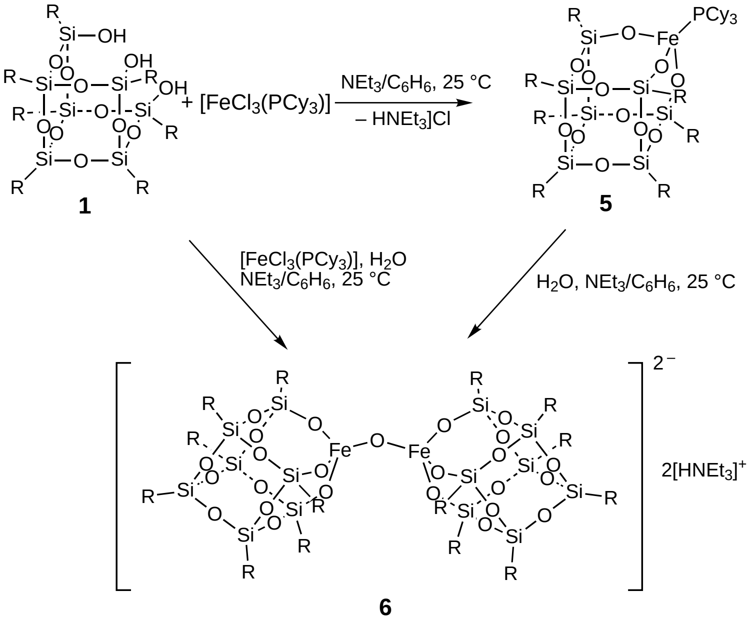

Scheme 2. Synthesis of compounds **5** and **6**, R = *c*-C_5H_9.

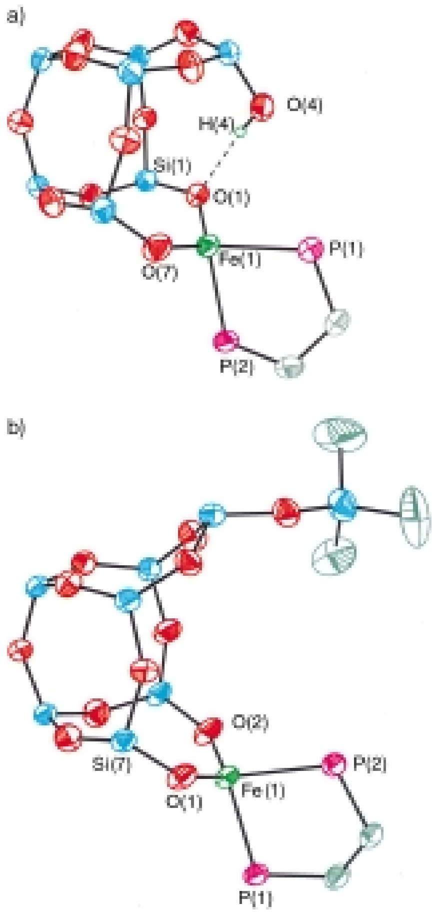

Figure 1. Molecular structures of **3** and **4**. a) **3**·0.5 C_6H_6, selected bond lengths [Å] and angles [°]: Fe(1)-O(1) 1.907(3), Fe(1)-O(7) 1.869(3), Fe(1)-P(1) 2.486(1), Fe(1)-P(2) 2.469(1); O(1)-Fe(1)-O(7) 121.2(1), P(1)-Fe(1)-P(2) 83.74(4), Fe(1)-O(1)-Si(1) 130.6(2). b) **4**·1.5 C_6H_6, selected bond lengths [Å] and angles [°]: Fe(1)-O(1) 1.873(3), Fe(1)-O(2) 1.866(2), Fe(1)-P(1) 2.460(1), Fe(1)-P(2) 2.434(1); O(1)-Fe(1)-O(2) 122.3(1), P(1)-Fe(1)-P(2) 83.48(3), Fe(1)-O(1)-Si(7) 137.48(15). The cycloalkyl groups, benzene molecules, and hydrogen atoms have been omitted for clarity. Si: turquoise, oxygen: red, iron: green, carbon: gray, and phosphorus: magenta.

The IR spectra of these complexes indicate strong C–H stretching and bending vibrations displayed at 2950, 2870, and 1450 cm^{-1} for the CH_2 groups in the cyclopentane rings as well as a strong Si–O streching band centered at 1120 cm^{-1}. The features in the region 1000–800 cm^{-1} correspond to the Si–C and Si–O stretching, and the C-C-H bending vibrations, which are similar to those observed in a tin–silasesquioxane complex[8a] and in zeolites.[8b] An O–H stretching vibration is observed at 3150 cm^{-1} in the IR spectrum of **3**. The structures of **3**–**5** were determined by single-crystal X-ray diffraction. Similar bond lengths and angles were observed in the crystal structures of **3** and **4** (Figure 1).[9a, 9b] The iron(II) centers in the complexes have a distorted tetrahedral coordination geometry similar to that found in the [$FeCl_2$(dcpe)] precursor. The Si–OH group in **3** is clearly bent towards one bridging oxo oxygen atom (O(1)) and forms an intramolecular hydrogen bond. The H(4)···O(1) (1.947 Å), O(1)–O(4) (2.743 Å) distances, and the O(4)-H(4)···O(1) (172.7°) angle are very similar to those observed for hydrogen bonds in alcohols.[10] Further evidence for hydrogen bonding comes from the IR spectrum (see above). A similar intramolecular hydrogen bond has been reported by Duchateau et al. in an aluminum–silasesquioxane complex.[11] The Fe(1)···O(4)(H) distance in **3** is 3.66 Å and the Fe(1)···H(4)(O) distance was determined to be around 3 Å (based on the idealized hydrogen atom position). The Fe(1)···O($SiMe_3$) distance in **4** (6.39 Å) is much longer than the Fe(1)···O(4)(H) distance in **3**. This longer distance is probably caused by steric interactions between the bulky $OSiMe_3$ group and the Fe^{II} center. Recently Abbenhuis and co-workers reported the synthesis of Pt analogues of **3** and **4** by the reaction of [$PtCl_2$(dppe)] (dppe = bis(diphenylphosphanyl)ethane) with **1** and **2**.[12] The single-crystal X-ray structure shows that [{(c-C_5H_9)$_7$$Si_7O_{11}$-($OSiMe_3$)}Pt(dppe)] has a similar structure to that of **4** except that the coordination geometry around the platinum center is distorted square planar.

The X-ray crystallographic characterization of **5** (Figure 2) indicates that the Fe^{III} center possesses a tetrahedral geometry which comprises of the three oxygen atoms from the silasesquioxane molecule and the phosphorus atom.[9c] The polyhedron defined by the Fe and Si atoms is distorted, presumably because of the larger ionic radius of Fe^{III} ions (0.64 Å) compared to Si^{IV} ions (0.41 Å).[13] The Fe–P bond (2.51(1) Å) is 0.28 Å longer than the sum of the Fe and P covalent radii (2.23 Å). This long Fe–P bond can be attributed to the low affinity of the soft phosphane ligand toward the hard metal center.

Compound **5** exhibits some interesting reaction chemistry with water (Scheme 2). The treatment of solutions of **5** in benzene with a slight stoichiometric excess of water in the presence of NEt_3 leads to the formation of the μ-oxo-bridged dianion **6**. Compound **6** could also be prepared by the reaction of **1** with [$FeCl_3$(PCy_3)] in the presence of H_2O and NEt_3. The single-crystal X-ray analysis of **6** (Figure 2) revealed that the bridging oxo ligand lies on a twofold rotation axis.[9d] The distances and angles in the μ-Fe-O-Fe core are typical of

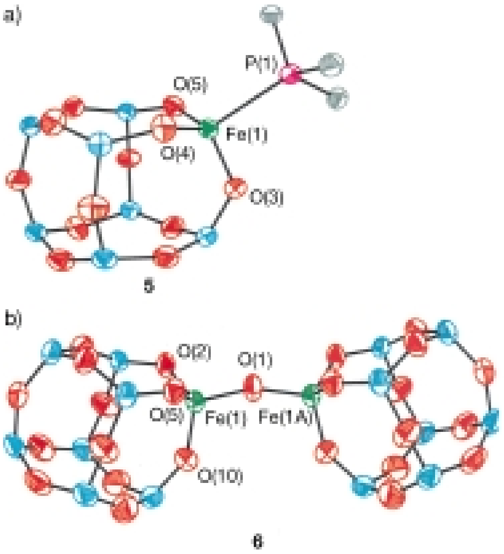

Figure 2. Molecular structures of **5** and **6**. a) **5** · C_6H_6, selected bond lengths [Å] and angles [°]: Fe(1)-P(1) 2.5070(11), Fe(1)-O(3) 1.829(3), Fe(1)-O(4) 1.818(3), Fe(1)-O(5) 1.824(2); P(1)-Fe(1)-O(3) 105.25(8), O(3)-Fe(1)-O(4) 110.74(12). Cycloalkyl groups on Si and the benzene molecule have been omitted for clarity. Only the three *ipso*-carbon atoms of the cyclohexyl groups of the phosphane are shown. Si: turquoise, oxygen: red, iron: green, phosphorus: magenta, carbon: gray. b) anion of **6**, selected distances [Å] and angles [°]: Fe(1)-O(1) 1.790(2), Fe(1)-O(2) 1.873(5), Fe(1)-O(5) 1.882(5), Fe(1)-O(10) 1.870(5), Fe(1)-Fe(1A) 3.502(3); O(2)-Fe(1)-O(5) 109.0(2), O(1)-Fe(1)-O(2) 107.8(3), O(1)-Fe(1)-O(5) 108.3(3), O(1)-Fe(1)-O(10) 110.8(3), Fe(1)-O(1)-Fe(1A) 157.0(5). The cations, solvent molecules and cycloalkyl groups have been omitted for clarity. Si: turquoise, oxygen: red, and iron: green.

complexes with singly bridged μ-Fe-O-Fe cores.[14] The UV/Vis spectra of **6** exhibit strong absorptions between 219 and 245 nm, similar to those found by Solomon and co-workers in their extensive studies of the Fe-O-Fe core of *met*-hemerythrin model complexes.[15] Feher et al. have reported oxo-bridged Al-μ-O-Al and Si-μ-O-Al silasesquioxane compounds in which the X-ray analysis indicated Al/Si/O connectivity and the μ-oxo structure.[16] Literature examples of μ-oxo-bridged metal – silasesquioxane complexes are rare, and the μ-oxo-bridged iron compound **6** is one of the few examples of such a complex.

Preliminary attempts to use complexes **3** – **6** as simple models for iron – silicate oxidation catalysts were unsuccessful. The catalytic activities of complexes **3** – **6** towards direct benzene oxidation have been tested at 30, 60, and 100 °C using N_2O (1.03 MPa) as the oxidant. No phenol or other products were produced under these conditions. The complexes decomposed overnight at 100 °C under N_2O (1.03 MPa). Whereas the homogeneous titanium – silicate systems that are excellent models of the titanium – zeolite catalysts,[4] our results indicate that the soluble framework iron silicates do not model the catalytic chemistry of the iron – zeolite systems. This implies that the local structure of the catalytically active Fe center in these zeolite systems is different from that found in the framework iron – silasesquioxane compounds.

In conclusion, we have employed simple iron – phosphane precursors to prepare the first examples of framework iron – silasesquioxane complexes. Hydrolysis of the Fe^{III} compound yields a dimeric μ-oxo-bridged Fe^{III} compound. The Fe-POSS complexes which should model framework metal-zeolite centers are not good models for the extra-framework centers implicated in a number of heterogeneous catalysts. We are continuing to investigate the reactivity of additional iron silicates to model extra-framework metal ion sites.

Experimental Section

[$FeCl_2$(dcpe)],[17] [$FeCl_3(PCy_3)$][18] and **2**[3a] were prepared by published methods. Compound **1** was purchased from Aldrich and used as received. NEt_3 and CH_3CN were purified by distillation over Na/K and CaH_2, respectively.

3: A solution of [$FeCl_2$(dcpe)] (0.104 g, 0.19 mmol) in C_6H_6 (5 mL) was added to a solution of **1** (0.19 mmol) in C_6H_6/ NEt_3 (10 mL; 4/1 (v/v)) and the resulting solution was stirred for 12 h at 25 °C. After filtration the solvent was removed in vacuo to give a virtually quantitative yield of crude **3** as an amorphous white foam. Recrystallization from benzene/acetonitrile afforded **3** (0.23 g, 91 % yield); elemental analysis calcd for **3**, $C_{61}H_{112}O_{12}P_2Si_7Fe$: C 54.22, H 8.30, P 4.59, Fe 4.15; found: C 54.19, H 8.09, P 3.71, Fe 3.35.

4: Same procedure as for **3** but with **2** instead of **1** as a starting material. Yield 0.24 g, 88.9%; elemental analysis calcd for **4**, $C_{64}H_{120}O_{12}P_2Si_8Fe$: C 54.01, H 8.44, P 4.36, Fe 3.94; found: C 53.62, H 8.44, P 4.36, Fe 3.21.

5: A similar procedure was adopted as for the synthesis of **3** except the solution was stirred for 3 h before filtration. Complex **5** could be obtained as colorless crystals in 91 % yield after recrystallization. Elemental analysis calcd for **5**, $C_{53}H_{96}O_{12}PSi_7Fe$: C 52.69, H 7.95, P 2.57, Fe 4.64; found: C 53.80, H 7.85, P 2.83, Fe 3.71.

6: A similar procedure was adopted as for the synthesis of **5** except that NEt_3 was used without drying. After recrystallization, **6** could be obtained as colorless crystals in 92% yield. Elemental analysis calcd for **6**, $C_{82}H_{158}O_{25}N_2Si_{14}Fe_2$: C 47.44, H 7.62, N 1.35, Fe 5.40; found: C 48.51, H 7.64, N 1.31, Fe 5.57.

Crystal structure analyses: All crystals are colorless. In each case a crystal was attached to a glass fiber using a spot of silicone grease and then mounted from a matrix of mineral oil. The crystal was immediately placed on a Bruker P4/CCD/PC diffractometer ($\lambda(Mo_{K\alpha}) = 0.71073$ Å) and cooled to 203(2) K using a Bruker LT-2 temperature device. For further details see ref. [9]. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-139882 – 139885. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[9] a) $\mathbf{3}\cdot 0.5\,C_6H_6$, triclinic, space group $P\bar{1}$, $a = 15.8034(7)$, $b = 21.587(1)$, $c = 22.742(1)$ Å, $\alpha = 94.839(1)$, $\beta = 91.726(1)$, $\gamma = 103.303(1)°$; $V = 7513.5(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.230\,g\,cm^{-3}$, $\mu = 0.409\,mm^{-1}$, $1.8 < 2\theta < 53.0$. Final R factor was 0.0625 ($wR2 = 0.1514$) for 26531 observed reflections with $I > 2\sigma(I)$. b) $\mathbf{4}\cdot 1.5\,C_6H_6$, triclinic, space group $P\bar{1}$, $a = 14.3308(6)$, $b = 14.8489(9)$, $c = 23.540(1)$ Å, $\alpha = 72.963(1)$, $\beta = 78.816(1)$, $\gamma = 61.248(1)°$; $V = 4190.5(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.221\,g\,cm^{-3}$, $\mu = 0.387\,mm^{-1}$, $3.22 < 2\theta < 52.90$. Final R factor was 0.0585 ($wR2 = 0.1413$) for 4066 observed reflections with $I > 2\sigma(I)$. c) $\mathbf{5}\cdot C_6H_6$, triclinic, space group $P\bar{1}$, $a = 11.0417(5)$, $b = 14.3909(7)$, $c = 22.445(1)$ Å, $\alpha = 92.955(1)$, $\beta = 98.253(1)$, $\gamma = 107.244(1)°$; $V = 3354.1(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.274\,g\,cm^{-3}$, $\mu = 0.429\,mm^{-1}$, $1.8 < 2\theta < 46.6$. Final R factor was 0.0524 ($wR2 = 0.1379$) for 9003 observed reflections with $I > 2\sigma(I)$. d) $\mathbf{6}\cdot CH_3CN\cdot 2\,C_6H_6$, orthorhombic, space group $Pnma$, $a = 21.838(1)$, $b = 31.824(2)$, $c = 17.1990(8)$ Å; $V = 11953(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.264\,g\,cm^{-3}$, $\mu = 0.449\,mm^{-1}$, $2.6 < 2\theta < 53.0$. Final R factor was 0.1249 ($wR2 = 0.3333$) for 12087 observed reflections with $I > 2\sigma(I)$.

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A Graphite-Like Complex with Large Cavities Constructed with the Complex Ligand $[Ni^{II}(bpca)_2]$**

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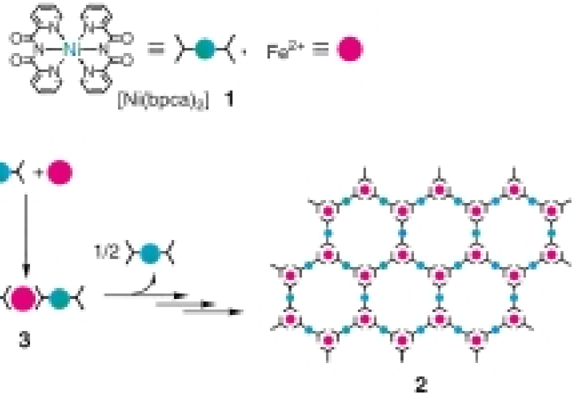
Recently metal complex assemblages have attracted much attention and several examples have been reported, including multiple helicates,[1] grids,[2] cages,[3] two-dimensional sheets,[4–6a, b] diamondoid networks,[7] and zeolite mimics.[8] In such compounds cooperative interactions between the metal ions often induce properties such as magnetism,[4–6b–h] conductivity,[9] and photoactivity.[6f–h] It has been shown that the use of a "complex ligand" as a building component is effective not only in the construction of the desired structures but also to design the spatial arrangement of metal ions, and to tune the metal–metal interactions. We have developed a strategy for constructing trinuclear and chain complexes by using $[M(bpca)_2]^{n+}$ as bis-bidentate complex ligands (where $n = 1$ for $M = Fe^{III}$; $n = 0$ for $M = Mn^{II}$ and Fe^{II}; Hbpca = bis(2-pyridylcarbonyl)amine).[10] Herein, we report the synthesis and structure of a two-dimensional coordination polymer constructed by the reaction of $[Ni(bpca)_2]$ (**1**) with iron(II) perchlorate (Scheme 1).



Scheme 1. Schematic representation for the formation of the honeycomb complex **2** by the reaction of **1** with iron(II) ion.

The reaction of **1** with iron(II) perchlorate hexahydrate in a 2:1 molar ratio afforded dark purple hexagonal prismatic crystals of $[Fe^{II}(\mathbf{1})_{1.5}](ClO_4)_2$ (**2**), a compound with a two-dimensional structure. Addition of one drop of water to the same reaction mixture afforded different deep violet crystals of the trinuclear species $[Fe^{II}(\mathbf{1})_2(H_2O)_2](ClO_4)_2$ (**3**) which is considered to be a precursor of **2**.

Figure 1 shows the two-dimensional honeycomb structure of **2**. The structure is that of a (6,3) net[11] in which the triply chelated iron(II) centers act as three-connected nodes (Figure 1 a). Each ring in a layer consists of six iron(II) ions at the corners and six units of **1** as the edges. The diagonal separations are Fe1#2 ··· Fe1#3 = 16.463(3) Å and Ni1 ··· Ni1#1 = 21.582(1) Å. The cavity size estimated from the space-filling model (Figure 1 b) is 12 Å along the Fe1#2 ··· Fe1#3 axis and 13 Å along the Ni1 ··· Ni1#1 axis. The whole structure of **2** is made up, as in graphite, of layers stacked upon each other along the c axis and related by crystallographical mirror planes at $c = 0$ and 0.5, hence the complete channel is formed along the c axis. The iron(II) centers are in a chiral environment formed by three chelating complex ligands, and a single layer consists of only one of the two optical isomers (Λ or Δ). It is to be noted that **2** has noninterpenetrating networks regardless of the presence of the large cavities.[4, 11] Interpenetration is prevented by the steric repulsion of the pyridine rings of the complex ligands. The perchlorate ions are located between the layers, half of them form two alternate

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